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Theory for equation of state of hard *D*-sphere fluid mixture

Shambhu Sharan Singh

Department of Physics, M S College, (B B A Bihar University), Motihari-845 401, Bihar, India

Abstract : The equation of state for a fluid mixture of hard *D*-sphere is discussed. The approach is based on the physical interpretation of the reciprocal of activity. Using the physical interpretation of the reciprocal of activity, an unified expression is derived for the equation of state of *D*-dimensional fluid mixture of hard *D*-spheres. The results for binary mixture of hard *D*-spheres are discussed.

Keywords : Fluid mixture, equation of state, dimensionality.

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1. Introduction

A fluid mixture of hard *D*-spheres is of current interest, because the hard *D*-sphere fluid mixture is as important in framing a theory of *D*-dimensional fluid mixture as the hard *D*-sphere fluid in case of *D*-dimensional one component fluid. The hard *D*-spheres are *D*-dimensional, incompressible hard spherical molecules (for example, $D = 1$ for one-dimensional hard rods, $D = 2$ for two-dimensional hard discs and $D = 3$ for three-dimensional hard spheres). It is a model, which is frequently used as a reference for developing a theory for the *D*-dimensional fluid. An approach based on a physical interpretation of the reciprocal of activity has been employed for hard sphere mixture [1] and for hard disc mixture [2]. This approach can be extended to a *D*-dimensional fluid mixture of hard *D*-spheres.

The purpose of the present investigation is two fold. First we derive unified simple expression for the equation of state for hard *D*-sphere mixture. Second we study the effect of dimensionality on the equation of state of the fluid mixture.

2. Basic theory

The chemical potential μ_α of the species α can be obtained from the partition function Q_N as [1,2]

$$\mu_\alpha = -kT\ln[Q_{N+1}/Q_N], \tag{1}$$

where Q_N for a *D*-dimensional fluid mixture is given by [3]

$$Q_N = \left[\prod_\alpha N_\alpha!\lambda_\alpha{}^{N_\alpha}\right]^{-1}\int\ldots\int\exp[-\beta U_N]\prod_{k=1}^{N} dr_k \tag{2}$$

with $$U_N = \sum_{\alpha,\gamma}\sum_{k<l} u_{\alpha\gamma}(k,l). \tag{3}$$

Here, $u_{\alpha\gamma}(k,l)$ is the pair potential between molecule k of species α and molecule l of species γ. λ_α is the thermal wavelength of species α, $\beta = (kT)^{-1}$ and N_α is the number of molecules of species α, such that the total number of molecules is $N = \sum_\alpha N_\alpha$.

Substituting eq. (2) in eq. (1), we get

$$\mu_i(\rho,T,X) = \mu_i^0(\rho,T,X) - kT\ln a_i^{-1}(\rho,T,X), \tag{4}$$

where $$\mu_i^0(\rho,T,X) = -kT\ln\left(\lambda_i^D/\rho_i\right); \tag{5}$$

and $$a_i^{-1}(\rho,T,X) = V^{-1}\int dr_{N+1}\exp\left[-2\beta\, u_{N+1,j}\right] \tag{6}$$

with $$u_{N+1,j} = (1/2)\sum_{\alpha,\gamma}\sum_{j=1}^{N_\alpha} u_{\alpha\gamma}(k,j) \tag{7}$$

is the potential energy of the $(N+1)$-th particle of species j within the fluid mixture.

Here, μ_i^0 is the chemical potential of an ideal gas of species i of density $\rho_i = \rho x_i$ and temperature T, where $\rho = N/V$ is the number density and $x_i = N_i/N$ is the concentration of species i, and a_i is the activity of the species i, relative to that of the ideal gas at the same temperature and density.

In order to perform the integration of eq. (6), the N particles are first fixed in a most likely configuration, then the $(N+1)$-th particle of species i wanders throughout whole system.

Other thermodynamic properties can be expressed in terms of a_i^{-1}. Thus, the pressure of a mixture is given by

$$\beta P/\rho = \sum x_i \left[1 - \ln a_i^{-1} + \rho^{-1} \int^{\rho} \ln a_i^{-1}(\rho', T, X) d\rho' \right]. \quad (8)$$

3. Hard D-sphere mixture

We consider a D-dimensional fluid mixture of additive hard D-spheres. We compute a_i^{-1} generalising the theory for the hard sphere mixture [1] and hard disc mixture [2]. a_i^{-1} is simply the probability that at a point $\boldsymbol{r}$ chosen at random $(N+1)$-th particle could be inserted. This probability is measured as the product of two terms $a_i^{-1} = P_1.P_2$. The first term is the probability that the point $\boldsymbol{r}$ chosen at random does not overlap one of the N particles of diameter d_{jj} in the D-dimensional space *i.e.*

$$P_1 = (V - N \sum_i x_i L_j)/V = 1 - \rho \sum_i x_i L_j, \quad (9)$$

where $L_j = V_D d_{jj}^D$ (10)

with [4]

$$V_D = \Pi^{D/2} / 2^D \Gamma(1 + D/2) \quad (11)$$

is the volume of a hard D-sphere of unit diameter and G (1) is the Gamma function.

The second term is the probability, condition to the first, that no particle will be in the remaining volume in which the $(N+1)$-th particle is to be accommodated. That additional volume in D-dimensional space is

$$S_{ij} = V_D \left[(d_{ii} + d_{jj})^D - d_j^D \right]. \quad (12)$$

Then the second probability P_2 that all N particles lie outside this volume S_{ij} is given by [2]

$$P_2 = \exp[-\rho \sum_i x_i S_{ij} / (1 - \rho \omega_i)], \quad (13)$$

where w_i is the average volume effectively excluded to a particle of species i by each particle in the mixture, when they are closed packed. Then a_i^{-1} is given by

$$a_i^{-1} = P_1 P_2 = (1 - \rho \sum_i x_i L_j) \exp[-\rho \sum_i x_i S_{ij} / (1 - \rho \omega_i)]. \quad (14)$$

The quantity w_i can be computed following the method of Andrews and Ellerby [1]. Thus

$$\omega_i = \omega_i^L + (\rho/\rho_0)\left(\omega_i^H - \omega_i^L\right), \quad (15)$$

where ω_i^L and ω_i^H are low and high density values of w_i, respectively and r_0 is the closed packed density. We can write $\omega_i^L = \sum_j X_j \omega_{ij}^L$ and $\omega_i^H = \sum_j X_j \omega_{ij}^H$, where w_{ij} is the average volume effectively excluded to a hard D-sphere of species i by hard D-sphere of species j in D-dimensional mixture. They can be evaluated following the method of Andrews and Ellerby [1]. Thus

$$\omega_{ij}^L = M_j \delta_j B_2^j. \quad (16)$$

where

$$M_{ij} = \left(3(2)^{2(D-1)}[B_3^j / (B_2^j)^2] - 1\right) / [2^D (2^D - 1)], \quad (17)$$

$$\delta_{ij} = (d_{ii}/d_{jj}) + 2^{-(D-1)}(1 - d_{ii}/d_{jj}) / M_{ij}, \quad \text{for } d_{ii}/d_{jj} < 1;$$
$$= 1 \quad , \text{for } d_{ii}/d_{jj} > 1 \quad (18)$$

and $\omega_{ij}^H = \rho_0^{-1}$. (19)

where B_2^{jj} and B_3^{jj} are, respectively, the second and third virial coefficients for hard D-spheres of species j. They are available for 2 £ D £ 5 [4]. Using these values of B_2^{jj} and B_3^{jj} we can calculate ω_{ij}^L. On the other hand, ω_{ij}^H can be obtained from the closed packed density r_0 and hence h_{cp} is the packing fraction h at r_0.

Finally, we obtain a simple expression for a_i^{-1} for the hard D-sphere fluid mixture

$$a_i^{-1} = (1 - cz)\exp\left[-\alpha_i Z / (1 - \beta_i Z - \gamma_i Z^2\right], \quad (20)$$

where $Z = \rho/\rho_0 = \eta/\eta_{cp}$, (21a)

$$c(D) = \rho_0 \sum_i x_i L_j, \quad (21b)$$

$$\alpha_i(D) = \rho_0 \sum_i x_i S_{ij}, \quad (21c)$$

$$\beta_i(D) = 1 + \gamma_i = \rho_0 \omega_{ij}^H. \quad (21d)$$

Here the packing fraction h is defined as

$$\eta = V_D \rho d^D = \rho V_D \sum_i x_i d_{ij}^D. \quad (22)$$

Substituting eq. (20) in eq. (8), we obtain an expression for pressure of hard-D-sphere fluid mixture

$$\beta P/\rho = \sum_i x_i \left[\alpha_i z/(1 - \beta_i z - \gamma_i z^2) - (cz)^{-1}\ln(1 - cz)\right.$$
$$- (\alpha_i / 2\gamma_i z)\ln(1 - \beta_i z + \gamma_i z^2)$$
$$\left. - (\alpha_i \beta_i / 2\gamma_i (1 - \gamma_i) z)\ln([1 - \gamma_i z]/[1 - z])\right] \quad (23)$$

The functional form of eq. (23) is similar to those found for two- and three-dimensional systems. It reproduces the corresponding results for hard sphere mixture [1] and hard-disc mixture [2].

4. Binary mixture of hard *D*-spheres

In this section, we employ the theory to a binary mixture of additive hard *D*-spheres. For such a system, α_i and β_i reduce to

$$\alpha_1(D) = \eta_{cp}\left(x_1(2^D - 1) + x_2[(1+R)^D - R^D]\right) / (x_1 + x_2 R^D), \quad (24)$$

$$\alpha_2(D) = \eta_{cp}\left(x_1[(1+R)^D - 1] + x_2[(2^D - 1)R^D]\right) / (x_1 + x_2 R^D), \quad (25)$$

$$\beta_1(D) = \gamma_1 + 1 = \beta_2(x_1 + x_2\delta_{12}R^D) / (x_1 + x_2 R^D), \quad (26)$$

$$\beta_2(D) = \gamma_2 + 1 = 2^{D-1}\eta_{cp}M_{ii}, \quad (27)$$

where $\delta_{12} = R^{-1} + 2^{-(D-1)}(1 - R^{-1}) / M_{ii}$ (28)

and $R = d_{22}/d_{11}$.

Using eq. (23), we calculate $\beta P/\rho$ for hard *D*-sphere mixture with $D = 4$ and 5, for $x_1 = x_2 = 0.5$ and $R = d_{22}/d_{11} = 1.1$. They are compared in Table 1 with the results obtained by Yadav and Sinha [3] using the perturbation theory. The agreement is good in low density. The hard *D*-sphere mixture is a model, for which experimental results are not available for comparison.

Table 1. $\beta P/\rho$, for binary mixture of hard *D*-sphere with $D = 4$ and 5 for $x_1 = x_2 = 0.5$ and $R = 1.1$.

η	$D = 4$		$D = 5$	
	Present theory	Yadav-Sinha	Present theory	Yadav-Sinha
0.10	2.219	2.210	4.272	4.041
0.15	3.329	3.269	8.643	8.024
0.20	4.948	4.823	10.296	13.661
0.25	7.799	7.115	43.296	25.201
0.30	12.411	10.524		
0.35	20.729	15.665		

Values of $\beta P/\rho$ for $2 \le D \le 5$ are reported in Figure 1 as a function of η for $x_1 = x_2 = 0.5$ and $R = 1.1$. We see that $\beta P/\rho$ increases with the dimensionality *D*. This is due to the fact that the molecules forming closed packing increases with *D*. Thus molecules are pushed closer together when *D* increases and hence density increases. For example, in a space of dimension $D > 3$, more molecules are pushed together in comparision to the three dimensional space. That is why, the thermodynamic properties increase when *D* increases.

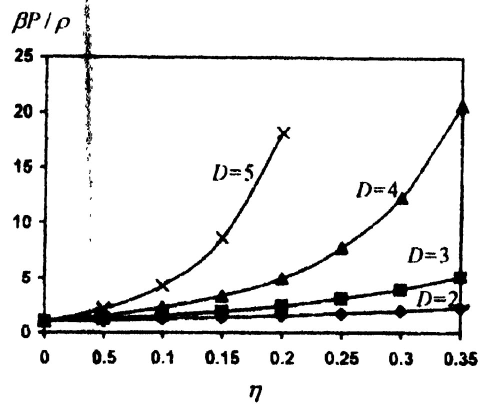

Figure 1. $\beta P/\rho$ for binary mixture of hard *D*-sphere as a function of η for $R = 1.1$ and $x_1 = x_2 = 0.5$.

5. Concluding remarks

It has been shown that the agreement with simulation data is fairly good for hard disc mixture [2] and hard sphere mixture [1] in low density range. It is expected that this simple expression yields good results even for $D \ge 4$. However, no comparison has been made for $D \ge 4$, since no simulation results are available.

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